

Studies on Electron Transfer Reactions: Oxidation of D-glucose by the Heteropoly 9-molybdomanganate (IV)

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ABSTRACT

Rates of electron transfer reaction of D-glucose with the heteropolyanion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ in aqueous medium have been studied spectrophotometrically at different temperatures. The order of the reaction with respect to substrate and oxidant is unity. The activation parameters are evaluated from the data. The sodium perchlorate has no effect on the rate of the reaction. The formation of Mn(II) ions are identified using EPR spectral technique.

Keywords: Heteropolyanion, Manganese(IV), EPR, Kinetics.

INTRODUCTION

Polyoxometalates have attracted much attention because of their structural versatility and use in different fields such as medicine, biology, catalysts and material science¹⁻⁴. This is particularly so with heteropolyanions containing higher valent transition ion as a heteroatoms. In contrast, Mn (IV) is present in a number of biologically important compounds⁵. Especially, it plays a vital role in photosystem (II) to produce molecular oxygen. Due to its interesting role in biological systems⁶, we have attempted to study the oxidizing property of Mn(IV) in the heteropolyanion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$, hereafter referred to as PA1. D-Glucose has been selected as the reductant due to its importance in food

supply and metabolism. There are several investigations on the oxidation of D-glucose by metal complexes, but there is no report on the oxidation of D-glucose by heteropolymanganate (IV). In this paper, the kinetics and mechanism of D-glucose by PA1 is presented.

EXPERIMENTAL

The compound PA1 was synthesised according to the literature method⁷. Ammonium heptamolybdate, manganese sulphate, sodium peroxy disulphate, sodium perchlorate and D-glucose were obtained from Qualigens, fine chemicals, India. All the chemicals were of AR grade and used without further purification. Doubly distilled water was used for kinetic measurements.

Sugar solutions were always used on the same day as made. Analar sodium perchlorate was used to study the effect of ionic strength.

ANALYTICAL AND PHYSICAL MEASUREMENTS

Molybdenum was estimated gravimetrically as oxinates⁸. Manganese was estimated spectrophotometrically⁸. IR spectrum was recorded on Perkin Elmer 783 spectrometer as KBr disks. Raman spectrum was recorded using DILOR 24 Raman spectrometer with spectra physics 164 Argon Laser (488 nm, 300mw), by pressing the sample into a solid matrix. To ascertain the oxidation state of manganese in PA1, EPR spectrum was recorded on Varian E112 spectrometer. DPPH was used as an internal field marker.

KINETIC MEASUREMENTS

The kinetic measurements were made using Hitachi model 200-20 UV-Vis spectrophotometer having thermostatically controlled cell compartment. The disappearance of UV maximum at 340nm was followed for PA1. pH measurements were made using Systronics 273pH meter. Several reaction mixtures with [PA] [Sugar] at fixed sulphuric acid concentration were prepared. After the completion of the reaction the unreacted manganese which existed in the form of Mn(II) in acid solution was estimated spectrophotometrically. In all cases the stoichiometry was found to be 2:1 [PA: Sugar].

PRODUCT ANALYSIS

One of the organic products, arabinose was identified by thin layer

chromatography. A solvent mixture of 1-Butanol-acetic acid- water (4:1:5) was used and the detection was carried out by using iodine crystals. The other product formic acid was identified by treating the product with Zn/HCl followed by the addition of chromotropic acid⁹. The oxidation state of manganese changes from (IV) to (II) as probed by EPR spectroscopy EPR of the reaction mixture recorded at various time intervals from the time of mixing of reactants, showed increase in the intensity of Mn(II) signal with time (Figure 1).

RESULTS AND DISCUSSION

Characterisation of PA1

PA1, a heteropoly anion (Waggoner type), has nine edge-sharing octahedra. In PA1, Mn(IV) is surrounded by six oxygen resulting in a MnO_6 octahedron¹⁰. The structure is further confirmed by using vibrational and EPR spectral techniques.

Vibrational spectroscopy

IR spectrum of PA1 recorded is given in Figure 2. Vibrational spectroscopy is a promising technique, to identify even tiny changes arising from anion-cation interaction¹¹ in polyoxometalates chemistry. It has been used to find out the group frequencies like X-O (X=hetero atom) in polyoxometalates. PA1 has *cis*- MoO_2 groups¹². Generally the compounds having *cis*- MoO_2 groups exhibit doublet in the vibrational spectrum. PA1 exhibits strong bands at 900-950 cm^{-1} which correspond to the stretching frequencies of *cis*- MoO_2 terminal bonds. The other bands at 700, 600, 550 and 400 cm^{-1} correspond to the edge sharing MO_6 octahedra. In Raman spectrum

also, PA1 exhibits (shown in Figure. 3) two bands at 959 and 925 cm^{-1} and these bands may be assigned to *cis*- MoO_2 groups. The other bands at 890, 876, 850 and 816 cm^{-1} are due to the vibrations of edge-sharing MoO_6 octahedra.

EPR spectroscopy

The EPR spectrum of PA1 (Figure 4) shows a weak signal at $g = 4$ and a strong signal at $g = 2$. In a crystal field, d^3 ion with octahedral geometry has $^4A_{2g}$ ground state, which gives an isotropic resonance at $g = 2$. Distortion and spin-orbit coupling split the ground quartet into two Kramer's doublets with the separation $2(D^2 + 3E^2)^{1/2}$, where D and E are axial and rhombic zero field splitting parameters¹³. Simplification occurs when the zero field tensor, D takes the limiting form $2D \ll h\nu$ or $2D \ll h\nu$ ¹⁴. EPR spectrum of PA1 (Figure 4) reveals that the axial parameter D takes the limiting form $2D \ll h\nu$, as shown by weak signal at $g = 4$ and a strong signal at $g = 2$.

The D value computed by using the equation $D = \sqrt{3/2 [(g\beta B_0)^2 - (2g\beta B_{\min})^2]}^{1/2}$ is 0.004 cm^{-1} for PA1. For this calculation g (2.01) value of PA1 was used. The D value thus obtained is indicative of the almost perfect MnO_6 octahedron in PA1. The EPR spectrum of PA1 also shows hyperfine splitting at the region $g = 2$, with the splitting constant $A_{\text{Mn}} = 79.7 \times 10^{-4} \text{ cm}^{-1}$.

Oxidation of D-glucose by PA1

Kinetic measurements were carried out under pseudo-first order conditions, $[\text{PA}] < [\text{D-glucose}]$, in aqueous medium by spectrophotometric method. All the reactions followed first order kinetics as judged by the linearity of plots of \log (absorbance) versus time.

Dependence on substrate concentration

The dependence of rate on substrate concentration was studied for PA1 at 30°C with $[\text{oxidant}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$ and $[\text{substrate}]$ ranging from $4.86 \times 10^{-3} \text{ mol dm}^{-3}$ to $8.39 \times 10^{-3} \text{ mol dm}^{-3}$. Plot of k versus $[\text{substrate}]$ was linear with a slope of unity (shown in figure 5), showing first order dependence on the concentration of D-glucose (Table 1) in the reaction with PA1.

Dependence on oxidant concentration

Mn(IV) species in acidic medium undergoes rapid protonation and becomes Mn(III) ¹⁵. In the present case the colour of the Mn(IV) solution changed from reddish brown to light yellow, when sulphuric was added. In addition, the absorbance value was appreciably reduced and stood constant, when sulphuric acid was added to the PA1 solution. However, no appreciable shift in λ_{max} was observed. The decrease in the absorbance value showed with increase concentration of the sulphuric acid. This shows that the Mn(IV) species in acidic solution gets protonated and become Mn(III) species. The dependence of rate on oxidant was studied for PA1 at 30°C with $[\text{D-glucose}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$ (Table 2). Oxidation of D-glucose by PA1 shows a first order dependence on $[\text{PA1}]$. The rate constants show an initial increase followed by a decrease as the concentration of the oxidant is increased. This may be due to the formation of the complex between the complex between the substrate and the polyanion containing the trivalent manganese (PA-Mn(III)). The concentration of the active species gets reduced by the complex formation. Similar

behavior has been observed in the oxidation of formaldehyde by Mn(III) pyrophosphate, maleic acid by Mn(III) sulphate and citric acid by Mn(III) acetate^{16,17}. The possible reactive species in sulphuric acid are $\text{Mn}(\text{OH})^{2+}$, $\text{Mn}(\text{HSO}_4)^{2+}$, $\text{Mn}(\text{SO}_4)^+$, $\text{Mn}(\text{SO}_4)^{2-}$ and $\text{Mn}(\text{OH})_3(\text{HSO}_4)_3^{3-}$ and their presence depends on experimental conditions¹⁷.

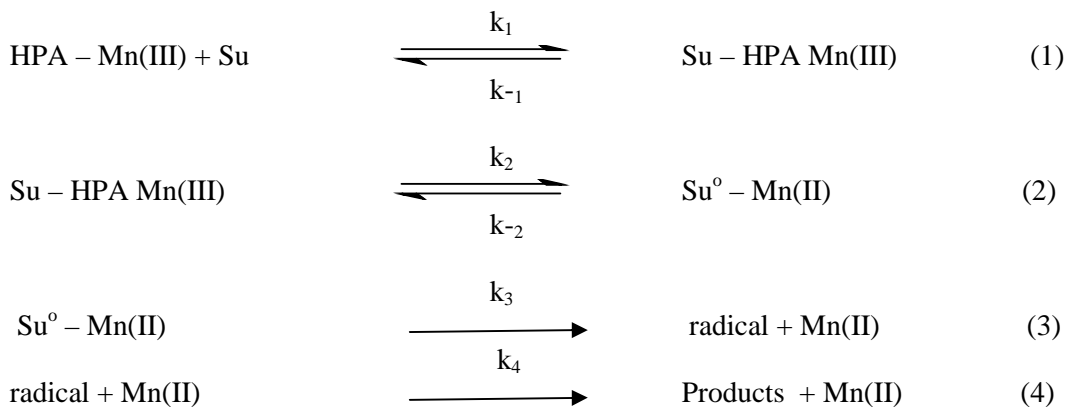
But in the present case, since Mn(III) ion is encircled by other MoO_6 moieties, the formation of above mentioned reactive species may not be possible. The formation of PA-Mn(III) substrate complex seems to be the probable reason for decrease in the rate as the concentration of the oxidant is increased. Added Mn(II) salt had no effect on the rate of oxidation, suggesting that PA having Mn(III) was not in equilibrium with Mn(II) species in the oxidation. However the reaction was found to go through free radical intermediate as confirmed by the polymerization of acrylonitrile in the system.

Dependence on $[\text{H}^+]$

Acid dependence was carried out for PA1 with $[\text{oxidant}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{D-glucose}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$ and $[\text{H}^+]$

$= 0.2 - 1.5 \text{ mol dm}^{-3}$ at 30°C . The increase in the rate of oxidation of glucose with increase in $[\text{H}^+]$ in the reactions may be due to the formation of PA-Mn(III) species. The plot of k versus $[\text{acid}]$ for PA1 is given in the Figure 6. When the pH of the solution is above 4, the anion (PA1) is completely deprotonated. On the contrary, if the pH of the solution is below 4, the anion exists as two forms in the aqueous solution, viz $[\text{H}_m\text{MnMo}_9\text{O}_{32}]^{(6-m)-}$ and $[(\text{M})_n\text{H}_p\text{MnMo}_9\text{O}_{32}]^{(6-p-n)-}$.

The highly protonated species acts as active species in the aqueous solution. Since at higher acid concentration, the formation of protonated species increases, this increases the rate of a reaction for PA1. Although the Mn(III) species in aqueous solution is not stable at neutral pH, it is stabilized in sulphuric acid. So the formation of stable PA-Mn(III) is favoured as the concentration of sulphuric acid is increased. The same trend is observed in the oxidation of phenacyl bromides by manganese (III) acetate. Added sodium perchlorate has no effect on the rate of the reaction. Based on the experimental evidences, a possible mechanism may be proposed.



Scheme 1

The step I may be rate- determining for PA1.

Activation parameters

The effect of temperature on the rate of the reaction was studied at 30, 35 and 40 °C and ΔH^\ddagger and ΔS^\ddagger were evaluated from the data (Table 4). Increase of temperature accelerates the rate of the reaction indicating the formation of a stable activated complex. The negative value of ΔS^\ddagger indicates the orderliness of the reaction and the formation of more rigid activated complex. The low value of ΔH^\ddagger indicates the formation activated complex is easier in PA1.

Table 1. Effect of [Reductant] variation on rate of the reaction.

[Oxidant] = $4.86 \times 10^{-4} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ M}$, $T = 30^\circ \text{ C}$.

[Reductant] x $10^3/\text{mol dm}^{-3}$	$K_1 \times 10^3/\text{s}^{-1}$ for PA1
4.86	1.17
5.74	1.32
6.62	1.55
7.51	1.79
8.39	1.95
8.92	2.12
9.65	2.35

Table 2. Effect of [Oxidant] variation on rate of the reaction.

[Reductant] = $4.86 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ M}$, $T = 30^\circ \text{ C}$

[PA1] x $10^4/\text{mol dm}^{-3}$	$K_1 \times 10^5 \text{ s}^{-1}$
4.86	9.69
5.13	9.94
5.50	11.14
5.92	10.50
6.72	9.58
7.22	9.25
8.0	8.65

Table 3. Effect of varying acid strength on rate of the reaction.

[Oxidant] = $4.86 \times 10^{-4} \text{ mol dm}^{-3}$,
[Reductant] = $4.86 \times 10^{-3} \text{ mol dm}^{-3}$,
 $T = 30^\circ \text{ C}$

$[\text{H}^+]/\text{mol dm}^{-3}$	$K_1 \times 10^3/\text{s}^{-1}$ for PA1
0.2	1.2
0.3	1.4
0.4	2.1
0.5	3.0
0.7	4.5
0.9	5.7

Table 4. Effect of temperature on the rate of the reaction and activation parameters.

[Oxidant] = $4.86 \times 10^{-4} \text{ mol dm}^{-3}$, [Reductant] = $4.86 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ M}$.

Temp K	$K_1 \times 10^4/\text{s}^{-1}$ (PA1)	$\Delta H^\ddagger/\text{kJ mol}^{-1}$ (PA1)	$\Delta S^\ddagger/\text{JK}^{-1} \text{ mol}^{-1}$ (PA1)
303	8.06	46.4	172.1
308	11.70	46.4	172.2
313	20.90	46.3	169.2

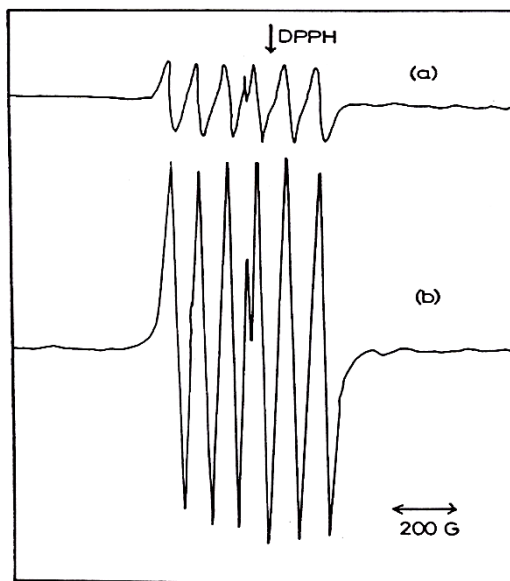


Figure.1. X-band EPR solution spectra of the product Mn(II), as a function of time (a) after 5 minutes and (b) after 10 minutes

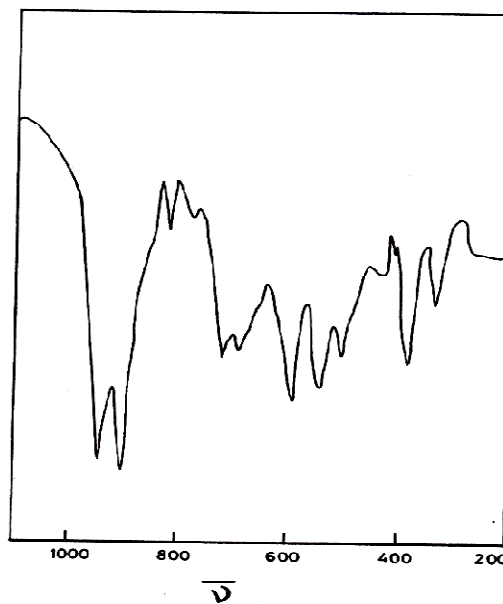


Figure.2. IR spectrum of the heteropoly anion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ as KBr disks. Ammonium is the counter cation for this anion.

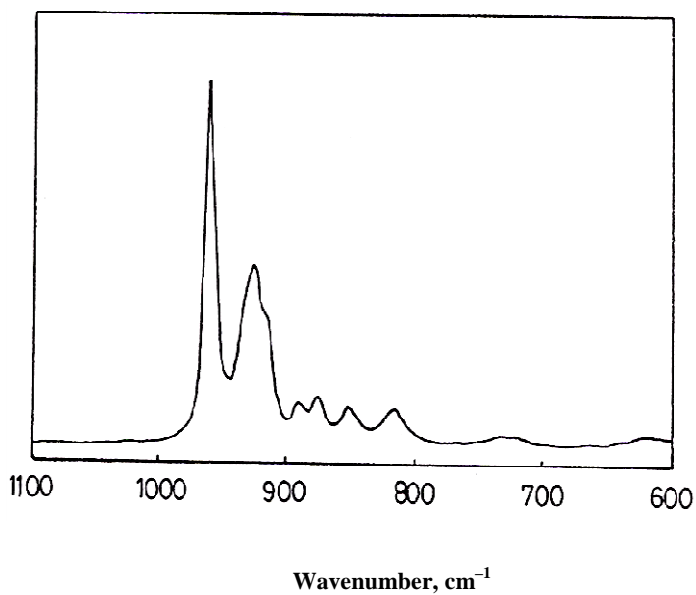


Figure.3. Raman spectrum of the heteropoly anion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$. Recorded by pressing the sample in the solid matrix. Ammonium is the counter cation for this anion.

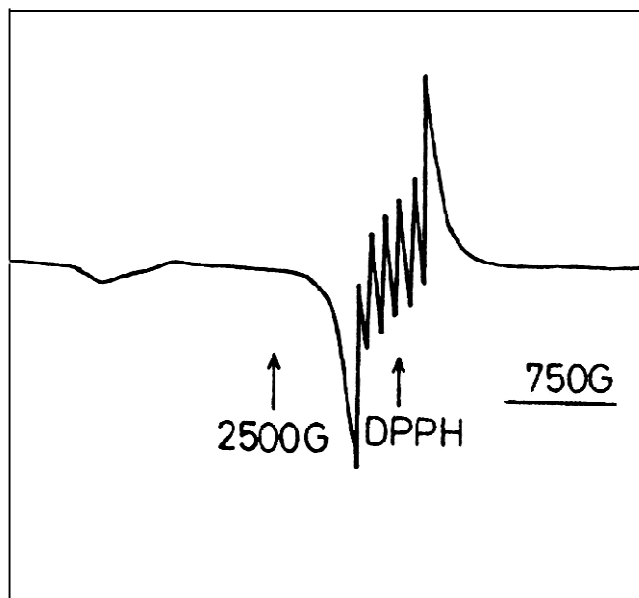


Figure.4. X-Band Polycrystalline EPR spectrum of Mn(IV) in HPA at 300 K

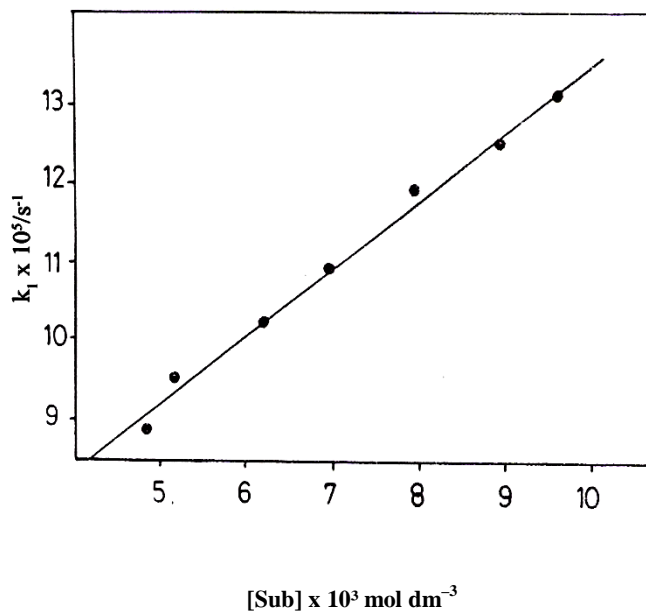


Figure.5. Plot of K versus substrate concentration for $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$. Other conditions : $[\text{reductant}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ mol dm}^{-3}$ and $T = 30^\circ$

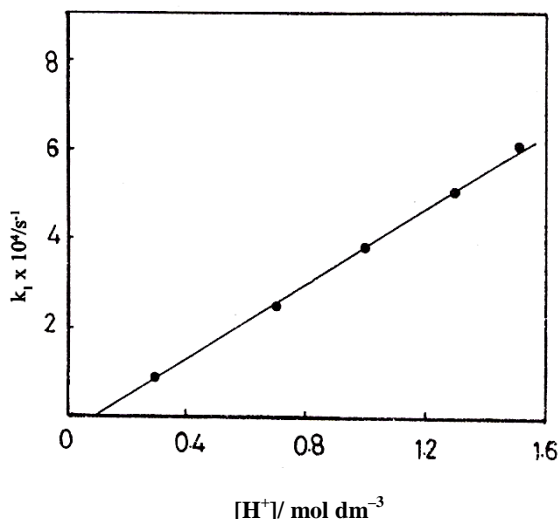


Figure.6. Plot of k versus acid strength concentration for $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$. Other conditions : $[\text{reductant}] = 4.86 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{oxidant}] = 4.86 \times 10^{-4} \text{ mol dm}^{-3}$ and $T = 30^\circ$

CONCLUSION

The heteropolyanion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ undergoes one electron reduction with D-glucose in aqueous medium at different temperatures. The one electron transfer proceeds through free radical mechanism. For the reduction of 2 moles of HPA, 1 mole of D-glucose is consumed. The organic products are arabinose and formic acid. Order with respect to [HPA] is one and order with respect to [D-glucose] is also one.

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